Restructuring of silver catalysts after oxidation reactions – looking beneath the surface

Dr Tina Bergh[1], Youri van Valen[1], Jia Yang[1], Ole H. Bjørkedal[2], Ann Kristin Lagmannsveen[3], Hilde J. Venvik[1]

[1]Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, [2]Dynea AS, Lillestrøm, Norway, [3]K.A. Rasmussen, Hamar, Norway

Introduction

The silver catalysed partial oxidation of methanol is one of the most used industrial processes to produce formaldehyde globally [1]. The industrial catalysts take the form of unsupported silver particles, but it is not possible to run under differential conditions with a particle bed setup at a lab scale. Therefore, we instead use an annular reactor that enables operating at low oxygen and methanol conversions, isothermal conditions and suppressing unwanted gas phase reactions [2]. We study the methanol to formaldehyde reaction and its sub-reactions including oxidation of CO and H_2, with and without water in the feed. At elevated temperatures, oxygen dissolves into the silver, the silver restructures, and pinholes form [3]. Electron microscopy techniques enable us to get a complete view of the restructuring that extends beneath the silver surface. We aim to understand the structural changes as a function of the gas mixture and couple this to the kinetic studies.

Methods

Silver cylinders (Ø 10 mm, 10-20 mm length) were machined from rods (Goodfellow) and placed inside a narrow quartz tube reactor that extended upstream to ensure low path length and linear flow. Fresh silver catalysts were exposed continuously as they were heated up and held for 12, 36 and 84 h at furnace setpoints in the range of 620-650 °C. Gas chromatography enabled quantification of all products except for H_2O. Microstructural characterisation of the catalysts was done after subsequent cooling. For comparison, also fresh silver catalysts and catalysts heated in inert gas and air were characterised. Scanning electron microscopy (SEM) enabled studying large areas of the catalyst surfaces. Focused ion beam (FIB)-SEM tomography, slice-and-view, provided three-dimensional views of the silver grains and enclosed cavities beneath the surface. Further, we prepared cross-sectional lamellae using FIB, collected scanning precession electron diffraction (SPED) data in the transmission electron microscope and did orientation mapping using pyxem [4].

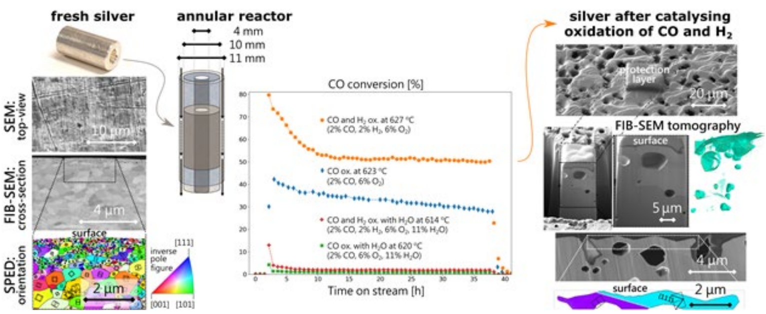
Results

The kinetic studies show that the conversion of CO is enhanced by H_2, while it is completely inhibited if H_2O is added to the feed. Moreover, the methanol conversion and selectivity towards formaldehyde increases with time if H_2O is added. The microstructural characterisation reveals that the fresh silver is decorated by surface scratches and has a nanocrystalline grain structure in the near-surface region. Drastic changes are seen after exposure to the various reaction atmospheres at elevated temperatures. All heated catalysts display larger grains with twins. Faceted pinholes and sub-surface cavities (Ø$\lesssim$10 µm) appear after oxidation of H_2 and syngas (CO and H_2), also with H_2O in the feed. For several catalysts, smaller rounded cavities down to a few nanometres in diameter can also be seen. Most of the heated silver catalysts show surface faceting and preferential exposure of {111} surface planes. An exception is the catalyst after methanol oxidation, which displays rounded surface features and no distinct faceting.

Conclusions

Kinetic data obtained from an annular reactor setup with cylindrical silver catalysts show how the catalyst activity changes with time in various gas mixtures. Microstructural characterisation using primarily FIB-SEM and SPED discloses the silver catalyst restructuring that has occurred after the different oxidation reactions. Distinct changes were documented in terms of grain structure, surface faceting and (sub)-surface pores. By combining the results from the characterisation and the kinetic studies, we explain how the reaction mixture and resulting restructuring affect the catalyst activity.

Graphic:



Keywords:

Silver catalyst; FIB-SEM tomography; SPED

Reference:

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